National Institute of Standards and Technology

Certificate of Analysis

Standard Reference Material® 2693

Sulfur and Mercury in Coal (Bituminous)

This Standard Reference Material (SRM) is intended primarily for use in the evaluation of techniques employed in the determination of sulfur, mercury, ash content, and calorific value ($MJ \cdot kg^{-1}$) in coal and materials of a similar matrix. SRM 2693 consists of 50 g of bituminous coal ground to pass a 250 µm (60 mesh) sieve, homogenized, and packaged in an amber glass bottle.

Certified Values: The certified values for sulfur and mercury, expressed as mass fractions [1] on a dry basis, are provided in Table 1. The certified values are based on a single NIST primary method. A NIST certified value is a value for which NIST has the highest confidence in its accuracy in that all known or suspected sources of bias have been investigated or accounted for by NIST.

Reference Values: The reference value for ash content [2] is provided in Table 2. This reference value is based on the statistical analysis by NIST of data from laboratories participating in the CANSPEX® 2002-4 interlaboratory study completed in November 2002 in conjunction with Quality Associates International, Ltd., Douglas, Ontario, Canada.[1] Reference values are noncertified values that are the best estimates of the true values; however, the values do not meet NIST criteria for certification and are provided with associated uncertainties that may reflect only measurement precision and may not include all sources of uncertainty.

Supplemental Information: Summary statistics reported by CANSPEX® for SRM 2693 are provided in the addendum of this certificate to demonstrate user experience with this material using conventional methods and to further characterize the matrix. The CANSPEX® 2002-4 results were not used in calculating the certified values for sulfur and mercury and should **NOT** be used as substitutes for NIST values.

Expiration of Certification: The certification of SRM 2693 is valid, within the measurement uncertainties specified, until **31 December 2016,** provided the SRM is handled in accordance with the instructions given in this certificate (see "Instructions for Use"). This certification is nullified if the SRM is contaminated or otherwise modified.

Maintenance of SRM Certification: NIST will monitor representative samples of this SRM over the period of its certification. If substantive changes occur that affect the certification before the expiration of this certificate, NIST will notify the purchaser. Registration (see attached sheet) will facilitate notification.

The coordination of the technical measurements leading to certification was performed by W.R. Kelly of the NIST Analytical Chemistry Division.

Willie E. May, Chief
Analytical Chemistry Division

Gaithersburg, MD 20899
Certificate Issue Date: 20 October 2004

Robert L. Watters, Jr., Chief
Measurement Services Division

[1]Certain commercial organizations, services, equipment, or materials are identified in this certificate to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by National Institute of Standards and Technology nor does it imply that the organizations, services, materials, or equipment identified are necessarily the best available for the purpose.

Certification analyses for sulfur were performed by W.R. Kelly, J.L.Mann, and R.D. Vocke of the NIST Analytical Chemistry Division. Certification analyses for mercury were performed by W.R. Kelly and S.E. Long of the NIST Analytical Chemistry Division. Homogeneity analysis was performed by A.F. Marlow, B.R. Norman, and J.R. Sieber of the NIST Analytical Chemistry Division. Moisture analyses were performed by J.L. Mann of the NIST Analytical Chemistry Division.

Statistical analyses leading to certified and reference values were performed by W.F. Guthrie of the NIST Statistical Engineering Division.

The support aspects involved in the issuance of this SRM were coordinated through the NIST Standard Reference Materials Program by B.S. MacDonald of the NIST Measurement Services Division.

The coal for this SRM was donated by Consol Coal Sales, Inc., Pittsburgh, PA.

INSTRUCTIONS FOR USE

Sampling: The unit should be thoroughly mixed by rotating the bottle before sampling. A minimum sample mass of 100 mg should be used for analytical determinations to be related to the sulfur and mercury values provided. The ash content was determined using a nominal sample mass of 1 g. The SRM should be stored in its original, tightly sealed bottle away from sunlight and intense sources of radiation.

Drying: In order to relate measurements to the certified and reference values that are expressed on a dry mass basis, users should determine a drying correction at the time of each analysis. The correction is determined by oven drying a separate 1 g sample in a nitrogen atmosphere at 107 °C ± 3 °C to a constant mass [3] or by an equivalent technique. For the purposes of certification, constant mass is operationally defined as the average mass of the first occurring three to five consecutive masses for which the absolute change in mass from one weighing to the next is less than the observed pooled standard deviation of the weighing of at least three gold wires included as controls, or the sample mass when the loss of mass reaches a slope of zero. Constant mass for this SRM was identified at the minimum (modeling the data using a polynomial fit and identifying the point where the first derivative vanishes) because this coal gained mass after initially losing mass during drying (*positive* behavior) [4]. During drying at NIST, the mass loss of SRM 2693 samples was observed to stabilize just before 1 hour. The average mass loss measured at NIST for SRM 2693 was 0.75 % (1s = 0.048 %, n = 9).

PREPARATION, HOMOGENEITY, AND ANALYSIS

Source and Preparation of Material: Approximately 320 kg of cleaned metallurgical coal was obtained from the Line Creek Mine of the Consol Coal Company in Sparwood, British Columbia, Canada. This multi-seam coal was crushed and air-dried prior to being pulverized and screened at 250 µm (60 mesh). The resulting fraction of clean coal, less than 250 µm, was divided into two portions using the spinning riffler technique. One portion was stored in bulk. The other portion was divided using the spinning riffler technique into the 50 g units and bottled.

Homogeneity Testing: Homogeneity testing by the NIST Analytical Chemistry Division is based on X-ray fluorescence spectrometric analysis of aliquots taken from 25 bottles, selected by stratified random sampling from the SRM 2693 lot. No evidence was found to indicate that the material is inhomogeneous for sulfur, or for 20 other elements with the possible exception of iron.

Analysis: The certified value for sulfur, reported in Table 1 as a mass fraction [1] on a dry basis (see "Instructions for Use") is based on measurements by isotope dilution thermal ionization mass spectrometry (ID-TIMS) [5].

The certified value for mercury, reported in Table 1 as a mass fraction [1] on a dry basis (see "Instructions for Use"), is based on measurements by isotope dilution cold vapor inductively coupled plasma mass spectrometry (ID-CV-ICP-MS) [6].

Table 1. Certified Values (dry basis) for SRM 2693

Element	Mass Fraction
S	0.4571 % ± 0.0067 %
Hg	37.3 µg/kg ± 7.7 µg/kg

The uncertainty in the certified values for sulfur and mercury is expressed as an expanded uncertainty, $U = ku_c$, calculated according to the methods in the ISO and NIST Guides [7]. The observed sulfur and mercury variations by isotope dilution methods were greater than expected for the analytical technique used. Therefore a prediction interval was used to account for the sulfur and mercury variabilities in this material [8]. The quantity u_c represents, at the level of one standard deviation, the combined effects of the uncertainties due to the measurement variability and material inhomogeneity. The quantity k is the coverage factor used to obtain an expanded uncertainty with an approximate confidence level of 95 %. For sulfur, the value of the coverage factor, $k = 2.31$, is determined from the Student's t-distribution with 8.35 degrees of freedom and a confidence level of 95 %. For mercury, the value of the coverage factor, $k = 2.31$, is determined from the Student's t-distribution with 8.14 degrees of freedom and a confidence level of 95 %.

Reference Values and Uncertainties: The reference value for ash content is based on data obtained from 43 laboratories using ASTM 3174 method [2] in the CANSPEX® 2002-4 Coal Round Robin.

Table 2. Reference Value (dry basis) for SRM 2693

Ash Content (mass fraction)	9.44 % ± 0.11 %

The uncertainty in the reference value for ash content is expressed as an expanded uncertainty, $U = ku_c$, calculated according to the methods in the ISO and NIST Guides [7]. A prediction interval was used to account for the potential variability in this material [8]. The quantity u_c represents, at the level of one standard deviation, the combined effects of within-laboratory measurement uncertainty, between-laboratory uncertainty, and material inhomogeneity. The quantity k is the coverage factor used to obtain an expanded uncertainty with an approximate confidence level of 95 %. For ash content, the value of the coverage factor, $k = 1.96$, was obtained from the standard normal distribution and a confidence level of 95 %.

REFERENCES

[1] Taylor, B.N.; *Guide for the Use of the International System of Units (SI)*; NIST Special Publication 811 (1995).

[2] ASTM D 3174-93, *Test Method for Ash in the Analysis Sample of Coal and Coke from Coal*; Vol. 05.05, ASTM Book of Standards, West Conshohocken, PA.

[3] ASTM D 5142-90, *Standard Test Methods for Proximate Analysis of the Analysis Sample of Coal and Coke by Instrumental Procedures*; Vol. 05.05, ASTM Book of Standards, West Conshohocken, PA.

[4] Mann, J.L.; Kelly, W.R.; MacDonald, B.S.; *Observations of Anomalous Mass-Loss Behavior in SRM Coals and Cokes on Drying*; Anal. Chem., Vol. 74, p. 3585 (2002).

[5] Kelly, W.R.; Paulsen, P.J.; Murphy, K.E.; Vocke, R.D.; Chen, L.-T.; *Determination of Sulfur in Fossil Fuels by Isotope Dilution Thermal Ionization Mass Spectrometry*; Anal. Chem., Vol. 66, p. 2505 (1994).

[6] Long, S.E.; Kelly, W.R.; *Determination of Mercury in Coal by Isotope Dilution Cold-Vapor Generation – Inductively Coupled Plasma Mass Spectrometry*; Anal. Chem., Vol. 74, p. 1477 (2002).

[7] ISO; *Guide to the Expression of Uncertainty in Measurement*, ISBN 92-67-10188-9, 1st Ed. International Organization for Standardization: Geneva, Switzerland (1993); see also Taylor, B.N.; Kuyatt, C.E.; *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*, NIST Technical Note 1297, U.S. Government Printing Office: Washington, DC (1994); available at http://physics.nist.gov/Pubs/.

[8] Hahn, G.J.; Meeker, W.Q.; *Statistical Intervals: A Guide for Practitioners*; John Wiley & Sons, Inc.: New York (1991).

Users of this SRM should ensure that the certificate in their possession is current. This can be accomplished by contacting the SRM Program at: telephone (30l) 975-6776; fax (301) 926-4751; e-mail srminfo@nist.gov; or via the Internet at http://www.nist.gov/srm.

Addendum

Standard Reference Material® 2693

Sulfur and Mercury in Coal (Bituminous)

CANSPEX® 2002-4 Coal Round Robin Results: SRM 2693 was included as an unknown in the November 24, 2002 CANSPEX 2002-4 Coal Round Robin. Summary statistics reported by CANSPEX are provided in the addendum to this certificate to demonstrate user experience with this material using conventional methods and to further characterize the matrix. The CANSPEX 2002-4 Coal Round Robin results should **NOT** be used as substitutes for the NIST values.

Gaithersburg, MD 20899
Issue Date: 20 October 2004

Summary of Analysis Reported by CANSPEX

CANSPEX® 2002-4 Coal Round Robin: NIST SRM 2693

Parameter	Consensus Value	ASTM Method Referenced for Reproducibility and Repeatability	ASTM Reproducibility Standard Deviation	CANSPEX Reproducibility Standard Deviation	ASTM Repeatability Standard Deviation	CANSPEX Repeatability Standard Deviation	Number of Labs	Number of Methods
Moisture wt %	0.81	ASTM D 3173	0.11	0.11	0.07	0.03	81	15
Ash wt % db	9.42	ASTM D 3174	0.18	0.06	0.11	0.03	81	10
Volatiles wt % db	22.29	ASTM D 3175	0.35	0.63	0.18	0.09	67	12
BTU/lb db	14026	ASTM D 5865	36	43	18	16	79	12
Carbon wt % db	80.51	ASTM D 5373	0.89	0.70	0.23	0.20	40	10
Hydrogen wt % db	4.44	ASTM D 5373	0.11	0.24	0.06	0.03	37	8
Nitrogen wt % db	1.23	ASTM D 5373	0.06	0.06	0.04	0.02	36	8
Sulfur wt % db	0.46	ASTM D 4239c	0.02	0.01	0.01	0.005	81	17
Pyritic Sulfur wt % db	0.021	ASTM D 2492	0.06	0.01	0.03	0.005	14	5
Sulfate Sulfur wt % db	0.009	ASTM D 2492	0.01	0.006	0.007	0.0002	6	4
Chlorine µg/g db	386	ASTM D 4208	102	33	34	7	33	13
Fluorine µg/g db	88	ASTM D 3761	5	16	5	1	14	5
Mercury ng/g db	36	ASTM D 3684	11	15	7	1	16	9
Selenium µg/g db	0.84	ASTM D 4606	0.13	0.55	0.09	0.02	8	5
Free Swelling Index (FSI)	7.5	ASTM D 720	1.0	0.5	0.5	0.5	29	4